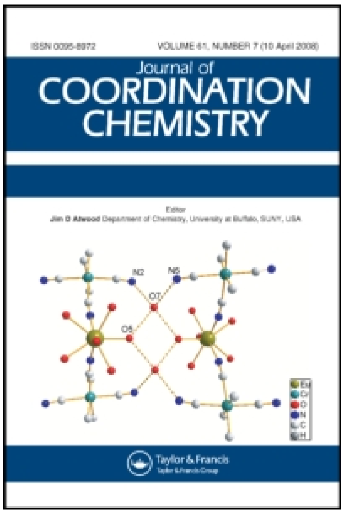

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X-RAY STRUCTURE OF THERMOCHROMIC *BIS*(*N*,*N*-DIETHYLETHYLENEDIAMINE)-COPPER(II)TETRAFLUOROBORATE

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The structure of a thermochromic complex, *bis*(*N*,*N*-diethylethylenediamine)copper(II) tetrafluoroborate $[CuL_2(BF_4)_2]$ having the lowest transition temperature (24°C) amongst its isomorphous counterparts (ClO_4^- salts of Cu and Ni) has been determined at 22°C thus offering a unique opportunity to study near transition structural parameters. The Cu atom at the crystallographic centre of inversion has square planar coordination from four N-atoms of two centrosymmetrically related ligands [Cu–N(secondary) = 2.061(5), Cu–N(primary) = 2.003(6) Å, bite angle N–Cu–N = 84.6(2)°], the diethyl group orientations insulate the metal ion from anion coordination [closest approach (Cu···F3 = 3.621(4) Å)]. The thermal anisotropies of the chelate ring carbons are normal and do not indicate any disorder, although the structure is determined at a temperature (≈22°C) very close to the transition. The highest thermal vibrations are shown by the BF_4^- anion and then to some extent by the terminal C-atoms of the diethyl groups. Factors involved in the thermochromic phase transition in these systems are discussed.

Keywords: Thermochromism; *N*,*N*-dialkyldiamine; Cu(II) complex; phase transition; X-ray structure

INTRODUCTION

Metal complexes exhibiting reversible discontinuous thermochromic transitions are of interest because of their varied application.[1–3] Among these, complexes with the ligand *N*,*N*-diethylethylenediamine (L) are perhaps the most interesting systems known to date. Although thermochromism of

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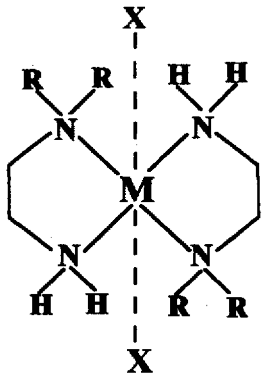
$CuL_2(ClO_4)_2$ **1** exhibiting a red to blue reversible colour change at ≈44°C, was first observed in 1938,[4] the thermochromic phase transitions of salts of BF_4^- **2** and NO_3^- **3** missed,[5] probably because the transition temperature (T_c) of the former was too low (≈24°C) and the latter too high (≈150°C).



1) $M=Cu$, $R=C_2H_5$, $X=ClO_4^-$
2) $M=Cu$, $R=C_2H_5$, $X=BF_4^-$
3) $M=Cu$, $R=C_2H_5$, $X=NO_3^-$
4) $M=Ni$, $R=C_2H_5$, $X=ClO_4^-$

Complexes with Cu and Ni salts of L, thermochromic only in the solid state, have been the subject of several spectroscopic investigations in order to understand the mechanism involved in the thermochromic transition.[6–11] Variable temperature Far-IR, IR and ESR spectroscopic studies interpret the colour change as being due to strengthening of axial anion coordination. However, the X-ray structure of **1** determined at temperatures below and above the transition temperature[12] clearly showed the anions to be far away from the metal-ion (>3.62 Å) in both the phases. Grenthe *et al.* on the basis of the large thermal motion of the chelate ring carbons perpendicular to the plane of the ring, explained[12] the mechanism in terms of dynamic inversion of the chelate ring weakening equatorial coordination. Amongst ML_2X_2 complexes, **2**, having the lowest T_c, is of special interest; the lowering of T_c in **2** was attributed to weaker H-bonding whereas the higher T_c's in **3** and **4** were thought to be the result of stronger interactions. In order to gain more insight into structure – thermochromic behaviour correlations, the title compound was synthesized and subjected to single crystal X-ray studies.

EXPERIMENTAL

Material

Diethylethylenediamine was purchased from Aldrich and used without further purification. All other materials used were of AR grade.

Preparation of the Complex

The title complex was prepared by adding dropwise *N*,*N*-Diethylethylenediamine (2 mmol) in ethanol to a stirred solution of copper tetrafluoroborate. The metal salt was prepared by adding excess of $CuCO_3$ to tetrafluoroboric acid (1 mmol) and adding ethanol (20 cm^3) upon completion

TABLE I Crystallographic details for the complex

Crystal data	
$[Cu(C_6H_{16}N_2)_2](BF_4)_2$	
$Mr = 469.58$	
Triclinic	
$P\bar{1}$	
$a = 8.0136(9)$ Å	MoKα radiation
$b = 8.6410(10)$ Å	$\lambda = 0.7107$ Å
$c = 9.7196(7)$ Å	Cell parameters from 25 reflections $\theta = 9{-}14°$
$\alpha = 65.735(11)°$	
$\beta = 66.498(8)°$	
$\gamma = 63.486(13)°$	$\mu = 1.103\ mm^{-1}$
$V = 529.6(9)$ Å^3	$T = 295(2)$ K
$Z = 1$	
$Dx = 1.472\ Mg\,m^{-3}$	
Data collection	
Enraf-Nonius CAD-4 diffractometer	$\theta max = 23°$
	$h = -7 \rightarrow 8$
$\omega/2\theta$ scans	$k = 0 \rightarrow 9$
Absorption correction: none	$l = -9 \rightarrow 10$
1468 measured reflections	3 standard reflections every 60 mins; no intensity decay
1468 independent reflections	
1360 observed reflections $[I > 2\sigma(I)]$	
Refinement	
Refinement on $\lvert F\rvert^2$	$(\Delta/\sigma)max < 0.001$
$R\,[F^2 > 2\sigma(F^2)] = 0.064$	$\Delta\rho(max) = 0.734$ e Å^{-3}
$R_w(F^2) = 0.184$	$\Delta\rho(min) = -0.505$ e Å^{-3}
$S = 1.155$	Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)
1456 reflections	
180 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	
H atoms refined as in riding model	

of the reaction to yield the desired solution of the metal salt, which was subsequently filtered to remove excess $CuCO_3$. The reaction mixture was then refluxed for 2 hours at about 40°C, then cooled in a refrigerator. The red product obtained was filtered, washed with ether and dried in a vacuum desiccator. Found: C, 30.9 H, 6.5 N, 11.9%. Calcd. for $C_{12}H_{32}CuN_4B_2F_8$: C, 30.8 H, 6.43 N, 12.01%. Crystals suitable for X-ray studies were obtained by slow evaporation of a methanolic solution of the complex.

X-Ray Crystallography

Crystallographic details of complex **2** are summarized in Table I. The structure was solved by the heavy-atom method and refined using full-matrix least-squares methods as given in Table I. The hydrogen atoms, located in a difference Fourier map, were refined using the riding model option in SHELX-93. Final positional parameters of non-hydrogen atoms along with their isotropic equivalent temperature factors are given in Table II. Computer programs used were, data collection: CAD-4 Software;[22] cell refinement: CAD-4 Software; data reduction: NRCVAX;[23] program(s) used to solve structure: SHELXS86;[24] program(s) used to refine structure: SHELXL93;[25] molecular graphics: ORTEP[13] and PLUTO.[26]

RESULTS AND DISCUSSION

An ORTEP[13] view of **2** is shown in Figure 1 and selected bond distances and angles are given in Table III. The Cu atom, at the centre of symmetry (0, 0, 0), possesses square planar coordination; closest approach of the two centrosymmetrically related BF_4^- anions to the metal centre is 3.621(4) Å [Cu···F3 (BF_4^-)] in a direction off by about 34° from the ideal axial vector perpendicular to the equatorial plane as observed in the isomorphous[14] structure **1**. In the high temperature (blue) form of **1** the metal occupies a two-fold site, the closest approach from two ClO_4^- ions (two-fold related) is longer [Cu···O(2) = 4.16(2) Å] than the low temperature form, but the Cu···O directions deviate less (maximum 22°) from the ideal axial directions. The Cu–N distances are dissimilar [Cu–N1 = 2.061(5), Cu–N2 = 2.003(6) Å], Cu–N (secondary) being longer than Cu–N (primary) as observed in the structure of **1** and in several substituted *N*,*N*-dialkyldiamine complexes.[15] The N1–Cu–N2 bite angle is 84.6 (2)°, which is also in close agreement with **1** and structures reported above. The bond distances and angles in the chelate ring are normal, although the C1–C2 bond [1.488(8)Å]

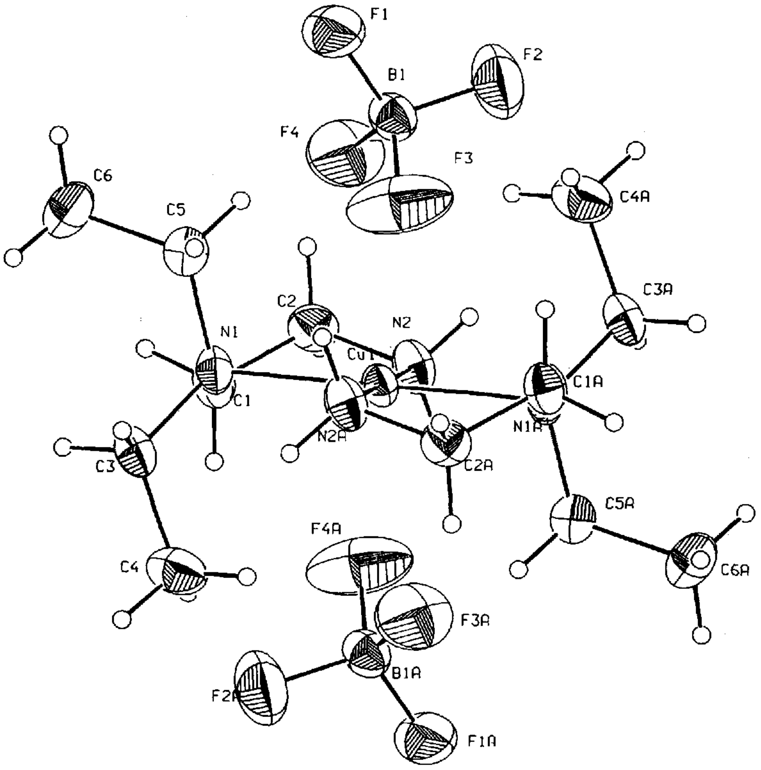


FIGURE 1 A perspective (ORTEP) view of **2** with thermal ellipsoids at the 50% probability level.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**. *U(eq)* is defined as one third of the trace of the orthogonalized *Uij* tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	0	0	0	41(1)
N(1)	691(7)	1171(7)	−2383(6)	49(1)
N(2)	1311(8)	−2329(7)	−563(6)	58(1)
C(1)	1298(10)	−274(9)	−3117(7)	56(2)
C(2)	2414(9)	−2045(9)	−2213(8)	59(2)
C(3)	−862(10)	2767(9)	−3003(8)	60(2)
C(4)	−2784(11)	2469(11)	−2394(11)	77(2)
C(5)	2360(10)	1720(10)	−2621(8)	61(2)
C(6)	3322(13)	2548(13)	−4301(10)	86(2)
B(1)	2420(11)	2813(10)	1646(10)	59(2)
F(1)	3507(7)	3914(6)	1127(8)	99(2)
F(2)	3035(11)	1363(8)	2799(8)	123(2)
F(3)	2484(11)	2258(12)	521(8)	134(3)
F(4)	543(9)	3751(10)	2240(13)	160(4)

TABLE III Selected bondlengths [Å] and angles [deg] for **2**

Cu(1)–N(2)	2.003(5)
Cu(1)–N(2)#1	2.003(5)
Cu(1)–N(1)	2.060(5)
Cu(1)–N(1)#1	2.060(5)
N(1)–C(3)	1.482(8)
N(1)–C(1)	1.489(8)
N(1)–C(5)	1.516(8)
N(2)–C(2)	1.467(9)
C(1)–C(2)	1.488(9)
C(3)–C(4)	1.514(10)
C(5)–C(6)	1.517(10)
N(2)–Cu(1)–N(2)#1	180.0
N(2)–Cu(1)–N(1)	84.6(2)
N(2)#1–Cu(1)–N(1)	95.4(2)
N(2)–Cu(1)–N(1)#1	95.4(2)
N(2)#1–Cu(1)–N(1)#1	84.6(2)
N(1)–Cu(1)–N(1)#1	180.0
C(3)–N(1)–C(1)	110.2(5)
C(3)–N(1)–C(5)	109.9(5)
C(1)–N(1)–C(5)	112.5(5)
C(3)–N(1)–Cu(1)	115.9(4)
C(1)–N(1)–Cu(1)	106.2(4)
C(5)–N(1)–Cu(1)	101.9(4)
C(2)–N(2)–Cu(1)	110.7(4)
C(2)–C(1)–N(1)	111.2(5)
N(2)–C(2)–C(1)	107.8(5)
N(1)–C(3)–C(4)	112.9(6)
N(1)–C(5)–C(6)	116.1(6)

Symmetry transformation used to generate equivalent atoms is #1: $-x$, $-y$, $-z$.

is shorter than the accepted C_{sp3}–C_{sp3} bond length (1.537 Å). A large decrease, *i.e.*, from 1.507(5) Å in the red form to 1.37(2) Å in the blue form was noted for **1** as a result of dynamic disorder in the ethylenediamine ring. However, thermal anisotropies of atoms C1 and C2 in **2** are within the normal range and do not suggest any disorder, although the measurements were carried out at a temperature only couple of degrees below the transition.

The chelate ring is in a 'half-chair' conformation and the atoms C1 and C2 deviate from the M–N–N plane by about 0.31 Å in opposite directions. The diethyl groups torsion angles Cu1–N1–C3–C4 [−47.9(8)°], Cu1–N1–C5–C6 [176.5(6)°] and their centrosymmetrically related counterparts create a situation where the approach of the BF_4^- anion is sterically hindered by the terminal methyl group C4 and the methylene group C5 (F3···H4B = 3.428 Å, F3···H5A = 3.152 Å) [Figure 1]. However, it is not always the case that these diethyl groups shield the metal ion from axially approaching anions. In fact, they can rotate freely creating situations where the coordination of as small an entity as water or as large an anion as acetate[16] to form a square pyramidal environment is possible. A remarkable example is where the dialkyls allow axial coordination resulting in octahedral geometry.[17] The steric nature of the dialkyl groups which can orient themselves either to insulate or to expose the metal centre to coordinating anions appears to be one of the significant features in deciding thermochromic behavior.[6,18] It is noteworthy that Cu(*N*,*N*-dimethylethylenediamine)$_2$(NO$_3$)$_2$ and Cu(*N*-isopropylethylenediamine)(BF$_4$)$_2$ are non-thermochromic.[19]

Molecular packing in **2** (Figure 2) shows the molecules as discrete units, probably to accommodate the structural changes involved during the phase transition. Both the hydrogens on N2 are involved in N–H···F type interactions with BF$_4^-$ anions; the two BF$_4^-$ anions form two H-bonded bridges between successive complex cations (Table IV). The H-bonding parameters in **2** are almost identical (as expected) to **1**, not conforming to the explanation that the lowering of the transition temperature in **2** could be because of weaker H-bonding as compared to **1**.[10] The lowering of T_c may well be because of the lighter centre of mass of the anion in **2** than in **1**, which starts thermal 'tumbling' at a lower temperature. As the X-ray intensity measurements are done at laboratory temperatures (22°C) close to the phase transition temperature of 24°C, an advantage naturally offered was to examine the 'near transition' behaviour of atoms. Therefore, the highest thermal

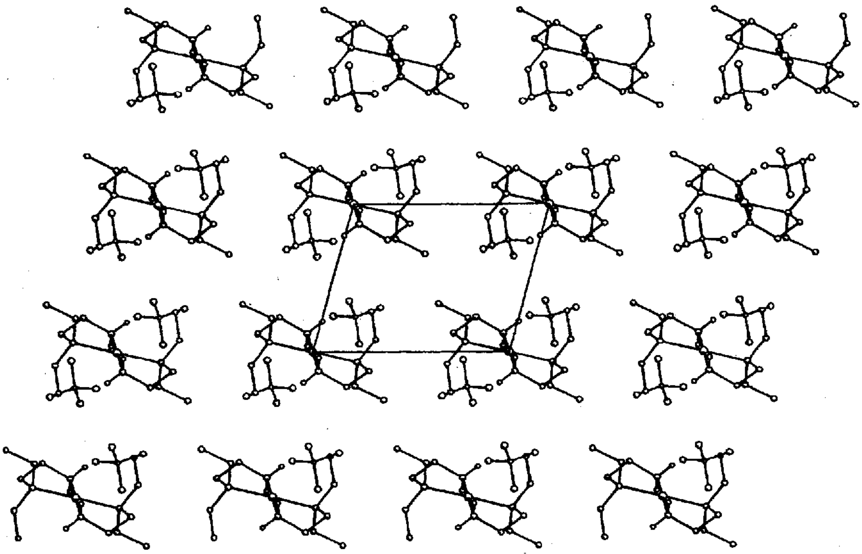


FIGURE 2 Packing of **2** viewed down the crystallographic *b* axis. H-atoms are shown only on N2 to show N–H···F contacts.

TABLE IV Hydrogen bonding data for the complex

$D–H\cdots A$	$H\cdots A$(Å)	$D\ldots A$(Å)	$D–H\ldots A$(°)
N2–H2A···F1^{i}	2.255(8)	3.026(7)	143.4(9)
N2–H2B···F3^{ii}	2.21(1)	3.000(1)	146.5(9)

Symmetry codes (i): $x, -1+y, z$; (ii): $-x, -y, -z$.

anisotropic displacements exhibited by the BF_4^- anion, the next higher vibrations shown by the terminal ethyl carbons C4 and C6 are significant in terms of the sequence of events that occur in the phase transition. This observation suggests that anions are the first to be disordered thermally, weakening the H-bonding links with the amino group of the ligand followed by the re-orientation of the ethyl group and the chelate ring inversion. The onset of sudden disorder of the chelate ring has been thought to be responsible for the thermochromic transition in **1**; it is interesting that the Cu- complex of *N*-isopropylethylenediamine with one of the chelate ring carbon atoms substituted by two methyl groups,[20] where the flipping of C1 and C2 is somewhat restricted, shows similar thermochromic behaviour (red $\rightleftharpoons$ violet at 101°C), while the *N*-isopropylethylenediamine complex is non-thermochromic.[19b] Another example in the same line is of a Cu complex with diazacyclooctane which exhibits first order thermochromic transition (orange $\rightleftharpoons$ violet at 90°C[21]). These examples imply complex conformational dynamics that take place during the phase transition in seemingly simple systems. These need to be investigated further by both experimental and theoretical methods and efforts in this direction are underway.

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[14] Unit cell parameters for complex **1**: $a = 8.0136(9)$, $b = 8.641(10)$, $c = 9.719(7)$ Å, $\alpha = 65.73(11)^\circ$, $\beta = 66.498(8)^\circ$, $\gamma = 63.486(13)^\circ$, $V = 529.57(9)$ Å^3 Complex **4**: $a = 8.098(3)$ Å $c = 9.795(5)$ Å, $\alpha = 63.73(4)^\circ$, $\beta = 65.31(5)^\circ$, $\gamma = 63.54(5)^\circ$, $V = 542.0(5)$ Å^3.

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